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Enzyme, Antibody, and Photocatalytically Active Nanoscale Scavengers and Sensors for CW and Biological Agents

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14. ABSTRACT

Thin films consisting of photoactive TiO2 and enzyme-functionalized polymer were studied for their activity against chemical agent simulants. The photochemistry of TiO2 was quantitatively studied for several molecules, including the activation of molecular oxygen which then oxidizes organic molecules. An important discovery is that the rate of the photoprocess is proportional to the square root of the ultraviolet light flux. The enzyme functionalized polymer films were produced to incorporate an indicator indicating that a specific chemical agent was being hydrolyzed. In addition methods to protect the polymer film from photooxidation on contiguous TiO2 surfaces were devised.Antimicrobial properties

15. SUBJECT TERMS

photochemistry, TiO2, chemical agent, antimicrobioal, polyquaternary amine, nanotubes, polydiacetylene, enzyme, antifungal, polymer enzyme conjugates

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a. REPORT	b. ABSTRACT	c. THIS PAGE			John Yates
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Report Title

Enzyme, Antibody, and Photocatalytically Active Nanoscale Scavengers and Sensors for CW and Biological Agents

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methods to protect the polymer film from photooxidation on contiguous TiO2 surfaces were devised.Antimicrobial properties of these films were studied.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

See edarlier progress reports

Number of Papers published in peer-reviewed journals: 52.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 10.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

FINAL REPORT – 42695-ch-MUR "Enzyme, Antibody and Photocatalytically Active Nanoscale Scavengers and Sensors for CW and Biological Agents"

The overall goal of the MURI research effort was to produce enzyme and TiO_2 –containing coatings for military vehicles which will destroy chemical agents and bioagents. The Russell laboratories was tasked with providing polymer-anchored enzyme scavengers and sensors for CW agents and polymer-anchored scavengers and sensors for BW agents. The Yates and Petek groups addressed the fundamentals of photochemistry on TiO_2 surfaces. The ultimate goal was to produce the basic information necessary to combine biochemically-based destruction with TiO_2 –based photocatalytic destruction reactions for CW and BW agents.

The subprojects and the results for both parts of the project are listed below:

BIOCHEMICAL APPROACH

Enzyme activity in coatings:

- An aqueous dispersion two component polyurethane coating was used to produce stable DFPase and OPH containing coatings.
- The enzymes were shown to retain up to 35% of their activity when incorporated into the coatings.
- The coatings retained significant activity for greater than 6 months at room temperature.
- Coatings were made containing both enzymes and TiO_2 which, with specific modifications, allowed both components to function.

Access of substrates to enzymes in coatings:

- The polyurethane coatings best suited to the goals of the project are nearly impermeable to the CW agents. To overcome the impenetrability of the polyurethanes pores in the material were produced through the use of porogens to provide access of substrates to the enzymes in coatings. Addition of 2% porogen to the coating mixture resulted in a 30% increase in substrate diffusion into the coating.

- Another successful approach was to modify the enzymes such that the concentrated themselves at the polymer surface. Hydrophobic modification of DFPase, by conjugation with a dimer/trimer mixture of uretdione, prior to immobilization in the coating resulted in a four fold increase in enzyme activity on the surface of the coating.

Rational protein modification leading to resistance of enzymes to TiO_2 and UV irradiation induced inactivation:

- UV light exposure inactivates enzymes but UV light is required to activate TiO_2. To reduce the effects of UV light on enzymes we developed a polymer sunscreen that is conjugated to the enzyme molecule to protect it from the UV irradiation.
- The free radical photoexcitation products TiO_2 oxidize biomolecules such as enzymes. A polymeric antioxidant was conjugated to the enzymes to protect them from oxidation.
- A combination sunscreen antioxidant polymer significantly increased the useful life of enzymes in coatings with TiO_2.

Selective capture of bacteria by modified coatings:

- Antibodies immobilized in polyurethane coatings were shown to selectively bind to target enzymes.
- Biotin binding proteins were used to bind to biotin modified anti-bacterial antibodies to the surface of a coating increasing the availability of the antibody.
- Anti-E. coli antibody bound to a coating surface selectively and tightly bound E. coli cells to the surface

Biocidal coating additives:

- Antimicrobial polyquaternary amines were synthesized that were highly antimicrobial.
- Polyquaternary amines incorporated in polyurethane coatings killed bacteria that touched the surface of the coating.
- The polyquaternary amines were shown to be effective for a wide range of bacteria

Biocidal Nanotubes:

- Polydiacetylene nanotubes with tertiary amine functional groups were synthesized in high yields.
- The nanotubes were effective at killing E. coli and B. subtilis in solution.
- The nanotubes displayed a color change reaction when heated or stressed marking them as potential detectors for bacterial contamination.

PHOTOCATALYTIC APPROACH

Role of surface defects on TiO_2:

- Surface defects were studied by various experimental methods. It was found that molecular O_2 adsorbs preferentially at oxygen-vacancy defect sites.

- It was also found that both CO and NO preferentially adsorb on surface defects and the binding energy was measured and calculated for these sites.

- The thermal decomposition of the mustard simulant, 2-chloroethyl ethyl sulfide, was studied on both TiO_2 powder and on single crystals of TiO_2. Lattice oxygen was shown to be involved in the photooxidation process.

- In contrast to reports in the literature, it was shown that UV irradiation does not produce oxygen vacancy defects.

- A new probe of surface defects on TiO_2 was devised, using the enhancement of bonding of CO_2 to these sites.

- A model for O-mediated vacancy diffusion on TiO_2, published by others in Science, was shown to be invalid.

Photooxidation of 2-CEES on TiO_2:

- Products CO, CO_2, carboxylate, formate and carbonate were observed and it was found that the Cl substitution in 2-CEES did not significantly affect these products.

- Photooxidation of 2-CEES leads to site poisoning for photooxidation as a result of oxidation product deposition on the surface.

Charge Transfer from TiO_2 to Electrophilic Molecules:

- Chlorine-containing organic molecules were found to accept electrons stored in trap sites near the bottom of the conduction band of TiO_2. Less electrophilic molecules of the same structure do not accept electrons.

- Photoproduced holes were shown initiate O_2 photodesorption from surface defect sites on TiO_2(110), and this reaction was shown to be effective for probing the fundamentals of photoexcitation due to its simplicity.

- Using the simple O_2 photodesorption from TiO_2 defect sites, it was shown that the rate of photodesorption is proportional to the square root of the light flux, not the first power, as expected. This was postulated to be due to the second-order electron-hole pair recombination reaction which dominates.

- The concentration of filled electron traps just below the conduction band was found to be diminished by water adsorption to produce surface Ti-OH groups.

- The number density of hole traps in a TiO_2 single crystal was measured. This number corresponded to about 30 ppm of the atomic sites in the crystal.

Doping of TiO_2 to Enhance the Absorption of Visible Radiation and to alter the Optical Properties of TiO_2:

- N-doping was shown to enhance the absorption of visible light, using a novel photocatalytic silver deposition process.

- Atomic H was shown to cause occupancy of electron traps near the bottom of the conduction band, working as an n-dopant. It was postulated that these states are about 0.1 eV below the band edge.

- A new optical technique to observe extremely tiny levels of atomic H doping of TiO_2 was devised and tested in several ways. It was applied to the dissociation of H_2 on Au/TiO_2 catalysts, and the kinetics and activation energy of the dissociation reaction were measured.

Two Photon Photoelectron Spectroscopy:

- Discovered Hydrated Electron on Metal Oxide Surfaces.

- Discovered Proton Coupled Electron Transfer at Methanol/TiO_2 Interface.

Review Articles:

- Two invited reviews were written in Topics in Catalysis (2005) and in Chemical Reviews(2006).

- A volume of Chemical Reviews entitled “Photochemistry and Photophysics on Surfaces (2006)” was coedited by J. T. Yates, Jr. and Hrvoje Petek.